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Efficiently photocatalytic reduction of carcinogenic contaminant Cr (VI) upon robust AgCl:Ag hollow nanocrystals

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ABSTRACT

Herein, we newly present a robust photocatalyst in terms of AgCl:Ag-Hollow nanocrystals (NCs) which exhibit fast photoreduction rate for representative carcinogenic contaminant (Cr (VI)) into the benign form(10 min). The provided hollow structure significantly enhanced light absorption and specific surface area (42 times than normal AgCl material), which are the two critical factors to improve the photoreduction activity. Further, the Schottky junction of the plasmonic system facilitates separation of photo-induced electrons and holes, which absolutely benefits the photocatalysis reactions. The photocurrent intensity, kinetic responses with apparent kinetic rate constant (k_{app}) and apparent quantum efficiency (AQE) (within 6 min) of AgCl:Ag-Hollow NCs were about 4–8, 5.3 and 2.7 times as that of normal AgCl material, respectively. Most strikingly, we anticipate such AgCl:Ag-Hollow NCs might become a promising candidate for practical application of water cleansing and environmental pollution purifying under visible light irradiation in the future.

1. Introduction

Over the past decades, semiconductor-based photocatalysis has been a hot research field due to its potential applications in coping with the energy crisis as well as environment pollution [1–6]. With unceasingly increasing industrial development after industrial revolution, carcinogenic hexavalent chromium (Cr (VI)) pollution incident continuously challenges our fragile living environment, especially the precious water resource that human beings live and depend on. It is well known that Cr (VI) is a frequent contaminant in wastewater arising from industrial processes such as leather tanning, paint making, electroplating and chromate production, etc. [7,8]. What troubled most is that the Cr (VI) ions can easily invade the human food chains and gradually accumulate to toxic levels, which becomes the main source of carcinogen and mutagenic primer [9]. Hence, multifarious conventional techniques for the removal of Cr (VI) have been reported, including biochemistry treatment, ion exchange, membrane separation, precipitation and adsorption, etc. [10]. Nevertheless, these approaches commonly subject to large requirement of chemicals, extra organic additives, high cost, and secondary pollution, all of which greatly hinder their practical applications. Consequently, pursuing environmental friendly and efficient technologies for cleaning Cr (VI)-containing wastewater has become an urgent task. Compared with those methods, photocatalysis has been proved to be a more attractive, efficient and clean strategy for reduction of toxic Cr (VI) species into the less harmful benign form, which is of paramount importance for human health [9,11].

Recently, there arose several research works concerning on photoreduction of Cr (VI) contaminants [12,13]. Unfortunately, those photocatalysts are far from commercial applications due to their long-term preparation process and low efficiency. To date, few works have been reported on plasmonic photocatalyst with well-defined morphology and excellent performance for photoreduction of Cr (VI) into the benign form. In this case, in the previous investigations, we have contributed a lot of theoretical and experimental efforts to study and improve the silver halide (AgX (X = Cl, Br, I)) based plasmonic photocatalysis, such as manipulation of the energy band structure and amelioration of the active crystal plane or hierarchical structure [11,14]. However, there still remains an immense

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space for further development of the AgX-based plasmonic photocatalysis [15,16]. To meet the high engineering requirements of the solar-powered sewage treatment, the catalytic efficiency and chemical durability of photocatalyst are the two key factors to be crucially solved [17,18]. Thanks to its facile plasmonic properties, superb photocatalysis properties and photo-stabilities, AgCl semiconductor material is considered to be one of the most promising candidates to break through this bottleneck [19,20].

Consequently, in the present work, we newly introduced a kind of AgCl:Ag-Hollow NCs which has been proved to be a robust plasmonic photocatalytic reduction agent to reduce the Cr (VI) into the Cr (III) via a facile and handy preparation approach. By means of the colorimetrical diphenylcarbazide (DPC) method [21], the photocatalytic activity for reduction of Cr (VI) contaminants has been investigated and showed that such NCs could facilely clean the Cr (VI)-containing waste water within 10 min. Furthermore, a novel and in-depth perspective of photocatalytic reduction mechanism for the reduction of Cr (VI) on the AgCl:Ag-Hollow NCs is proposed and discussed.

2. Experimental

2.1. Chemicals

Sodium chloride (NaCl) and Polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich and used without further purification. Silver nitrate ($AgNO_3$) and Potassium bichromate ($K_2Cr_2O_7$) were obtained from Sinopharm Chemical Reagent (Shanghai, China) and used as received. All aqueous solutions were prepared with ultra-pure water (>18.2 MΩ cm) from a Milli-Q Plus system (Millipore). All glassware used in the following procedures were cleaned in a bath of freshly prepared $HCl:HNO_3$ (3:1, aqua regia) and rinsed thoroughly by water prior to use.

2.2. Preparation of AgCl:Ag-Hollow NCs

The AgCl:Ag-Hollow NCs were prepared through a water soluble salt dissolution method according to previous reports with some modifications [19,20]. Briefly, $AgNO_3$ (0.17 g) and PVP (1.5 g) were dissolved in 20 mL absolute ethanol at ambient temperature with ultrasonication (the solution became deep brown). Then, the as-prepared NaCl saturated aqueous solution was injected into 100 mL absolute ethanol under vigorously magnetic stirring. Immediately, the white suspension granules were observed formed in the ethanol solution (NaCl cubic crystal). Soon afterwards, the above $AgNO_3$/PVP ethanol solution was poured into the NaCl ethanol suspension, and then, the mixture was around-the-clock stirred for 24 h to form NaCl@AgCl core–shell structure. Subsequently the obtained yellow colored NaCl@AgCl emulsion was placed into a breaker and irradiated by Xenon arc lamp (CHF-XM35-500 W, Beijing Trusttech Co. Ltd, China) light for 30 min to form NaCl@AgCl:Ag core–shell structure (the solution became purple). Finally, the purple suspension was treated by centrifugation (8500 rpm, 5 min) and the collections were washed with ultra-pure water for several times to remove PVP and residual ions (Na^+, NO_3^- and Cl^-), and the AgCl:Ag-Hollow purple NCs were achieved. For comparison, normal Ag/AgCl materials were prepared by mixing $AgNO_3$ (0.01 mol L^{-1}) and NaCl (0.01 mol L^{-1}) aqueous solution under stirring in ambient temerature. Some Ag NPs generated on the surface of AgCl during aforementioned Xenon arc lamp light irradiation. And the obtained Ag/AgCl material was denoted as AgCl-Normal for further control experiments.

2.3. Photocatalytic reduction hexavalent chromium

The carcinogen of Cr (VI) was photoreduced with as-prepared AgCl:Ag-Hollow NCs. In the whole process, the optical system for photoreduction was followed with similar that aforementioned above and equipped with a UV cutoff filter ($\lambda \geq 420$ nm), and the irradiation height was 15 cm. In a typical procedure, the as-prepared AgCl:Ag-Hollow NCs (20 mg) were well dispersed into 20 mL of Cr (VI) solution under ultrasonication (10 mg L^{-1} based on Cr (VI) in a dilute $K_2Cr_2O_7$ solution as the source of Cr (VI)) in a home-made reactor equipped with a cooling water circulator assembled to keep the whole reaction system maintaining at a constant temperature condition. Then, ethylene diamine tetraacetic acid (EDTA, 0.01 M) was injected into the mixture, and the pH of the reaction suspension was adjusted to 2.0 with $HClO_4$. Soon afterwards, the 0.02 M of color developing reagent of diphenylcarbazide (DPC) in acetone was added into the mixture, and the color of the mixture would turn into violet. The suspension was stirred for 30 min in the dark to reach adsorption–desorption equilibrium and then exposed to visible-light irradiation to start the photocatalysis. After the photoreduction experiment was triggered by irradiation of visible light, the solution of aliquots volume were periodically withdrawn from the reaction vessel and centrifuged to remove the photocatalyst powders. And the Cr (VI) reduction was measured based on the spectrophotometric colorimetrical DPC method (at $\lambda = 540$ nm) by using a UV-Vis spectrophotometer (ultra-pure water as reference). Normally, C_t is the concentration of Cr (VI) solution at time t, C_0 is the initial concentration (10 mg L^{-1}). The photocatalytic measurement mentioned above was repeated twice to ensure the reliability of the results. The reproducibility of the AgCl:Ag-Hollow NCs was also tested with the following procedure: the photocatalyst was washed with ultra-pure water and ethanol for several times after photoreduction and then retested in the fresh mixture solution of Cr (VI) under the same experimental conditions as mentioned above.

3. Results and discussion

3.1. Electronic images, crystal structure and photophysical properties

Morphology and element distribution of the as-prepared AgCl:Ag-Hollow NCs were investigated by SEM, TEM, HAADF-STEM and elemental mapping (Fig. 1). The mappings of present AgCl:Ag-Hollow NCs are colored to distinctly mark parts of the element distribution in this structure. Compared with the solubility of NaCl in water (26.5 wt%, 20 °C), its solubility in absolute ethanol (0.065 wt%, 20 °C) is much lower. Base on the fact, when a small amount of saturated aqueous solution of NaCl was injected into the absolute ethanol with ration volume, the reaction system would quickly turn into white color originated from precipitate of NaCl crystal. Subsequently, the $AgNO_3$/PVP in absolute ethanol was poured into the above-mentioned dispersion under vigorously magnetic stirring. Herein, PVP served as the capping agent to stabilize the generated AgCl particles and prevent agglomeration of the resultant [22]. The Ag NPs were generated on the surface of AgCl under visible light irradiation (Fig. 1a). The SEM images of the AgCl:Ag-Hollow NCs with different resolutions are shown in Fig. 1b–d. It is observed that the AgCl:Ag-Hollow NCs depicted hollow cubic structure, which might be benefited from the crystal morphology of NaCl in the synthesis phase (Fig. S1 in Supporting information) [23]. Obviously, the AgCl:Ag-Hollow NCs displayed uniform morphology with some pores on the shells. The TEM images (Fig. 1e) and elemental mapping images (Fig. 1f–h) could clearly reveal that both the Cl and Ag elements distributed on the cubic shell instead of center, which further proved the hollow structure obtained in such a AgCl:Ag material. In addition, the SEM and TEM images of the as-prepared AgCl:Ag-Hollow NCs with high resolution were corresponding performed. The pore and Ag^0